PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference P27103PC01	FOR FURTHER ACTION	See Form PCT/IPEA/416
International application No. PCT/IB2004/051458	International filing date *(day/month/year)* 13.08.2004	Priority date *(day/month/year)* 14.08.2003
International Patent Classification (IPC) or national classification and IPC H01L31/032, H01L31/18		
Applicant RAND AFRIKAANS UNIVERSITY et al.		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 5 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:
   a. ☒ *sent to the applicant and to the International Bureau)* a total of 16 sheets, as follows:
      ☒ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).
      ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.
   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) , containing a sequence listing and/or tables related thereto, in computer readable form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

☒	Box No. I	Basis of the opinion
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☒	Box No. VII	Certain defects in the international application
☐	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
24.08.2005	12.12.2005
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INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/IB2004/051458

Box No. I Basis of the report

1. With regard to the **language**, this report is based on the international application in the language in which it was filed, unless otherwise indicated under this item.

   ☐ This report is based on translations from the original language into the following language , which is the language of a translation furnished for the purposes of:
   - ☐ international search (under Rules 12.3 and 23.1(b))
   - ☐ publication of the international application (under Rule 12.4)
   - ☐ international preliminary examination (under Rules 55.2 and/or 55.3)

2. With regard to the **elements*** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:

Description, Pages	
1-63	as originally filed
Claims, Numbers	
1-94	filed with telefax on 25.08.2005
Drawings, Sheets	
1/28-28/28	as originally filed

   ☐ a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing

3. ☐ The amendments have resulted in the cancellation of:
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

4. ☐ This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - ☐ the description, pages
   - ☐ the claims, Nos.
   - ☐ the drawings, sheets/figs
   - ☐ the sequence listing *(specify)*:
   - ☐ any table(s) related to sequence listing *(specify)*:

* *If item 4 applies, some or all of these sheets may be marked "superseded."*

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/IB2004/051458

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Yes:	Claims	10-12,15,22,23,34,39,42,43,52,53,56,58,61,71-76,81,93,94
	No:	Claims	1-9,13,14,16-21,24-33,35-38,40,41,44-51,54,55,57,59,60,62-70,77-80,82-92
Inventive step (IS)	Yes:	Claims	
	No:	Claims	1-94
Industrial applicability (IA)	Yes:	Claims	1-94
	No:	Claims	

2. Citations and explanations (Rule 70.7):

see separate sheet

Box No. VII Certain defects in the international application

The following defects in the form or contents of the international application have been noted:

see separate sheet

Re Item V.

1) INDEPENDENT CLAIMS 1 AND 44

The present application does not meet the criteria of Article 33(1) PCT, because the subject-matter of claim 1 is not new in the sense of Article 33(2) PCT.
Document D1 discloses (see D1, Fig. 1 and 3, and references to D2 and D3 for the details of the method): a method of producing a IB-IIIA-VIA quaternary alloy semiconductor, namely Cu(InGa)(SeS)2, by (I) providing a metal comprising a mixture of IB and IIIA metals, (II) heating the metal in an atmosphere containing an element VIA (H2Se), thus forming a mixture of I-III-VI and I-III and III-VI alloys (see D2, cited in D1 as ref. 11 for the details of steps (I) and (II), page 180, line 23- page 181, end), (III) heating the obtained film in an atmosphere containing a second element VI (H2S), (IV) heating the obtained film, thus forming a quaternary or higher alloy semiconductor (Cu(InGa)(SeS)2).
The subject-matter of claim 1 is therefore not new and this claim is not allowable under Art. 33(1), (2) PCT.

Document D1 and D2 (see D2, fig. 3 and page 180) also disclose the subject-matter of independent claim 44 which is therefore not new and not allowable (Art. 33(1), (2) PCT).

2) The subject-matters of claims 2-9, 13, 14, 16-21, 24-33, 35-38, 40, 41, 45-51, 54, 55, 57, 59, 60, 62-70, 77-80 and 82-92 is also disclosed by document D1 (see D1, above-cited passages), therefore these claims do not add anything new to the claim 1 from which they depend, and they are not allowable under Art. 33(1), (2) PCT.

3) Dependent claims 10-12,15, 22, 23, 34, 39, 42, 43, 52, 53, 56, 58, 61, 71-76, 81, 93 and 94 do not contain any features which, in combination with the features of any claim to which they refer, meet the requirements of the PCT in respect of inventive step (Article 33(1) and (3) PCT).

4) All the claims meet the PCT requirements regarding industrial applicability.

Re Item VII.

Claims 1, 2, 18-20, 24-27, 36, 43, 44, 45, 66, 67, 81, 82 and 94 do not meet the requirements of Article 6 PCT in that the matter for which protection is sought is not clearly defined. The claims attempt to define the subject-matter in terms of the result to be achieved, which merely amounts to a statement of the underlying problem, without providing the technical features necessary for achieving this result. The coexistence of binary, ternary or quaternary alloys in the intermediary film(s), the fact that the molar ratio of particular alloy comprised in the intermediary film is kept constant during a step of the process, the obtention of a quaternary alloy in the final stage, etc... results from the parameters of the process (precursors, concentrations, temperatures, times, etc...) of the method and can not be used to define the technical features of the process.

Also, in claims 44, it is not clear how a quaternary alloy can be obtained, since the wording of the claim does not mention providing four elements. A technical feature essential to define the invention as described has been omitted. (Art. 6 PCT.)

Claims

1. A method for producing a group IB-IIIA-VIA quaternary or higher alloy semiconductor film, the method comprising the steps of:

   (i) providing a metal film comprising a mixture of group IB and group IIIA metals;

   (ii) heat treating the metal film in the presence of a source of a first group VIA element (said first group VIA element being hereinafter referred to as VIA_1) under conditions to form a first film comprising a mixture of at least one binary alloy selected from the group consisting of a group IB-VIA_1 alloy and a group IIIA-VIA_1 alloy; and at least one group IB-IIIA-VIA_1 ternary alloy,

   (iii) heat treating the first film in the presence of a source of a second group VIA_2 element (said second group VIA element being hereinafter referred to as VIA_2) under conditions to convert the first film of step (ii) into a second film comprising at least one alloy selected from the group consisting of a group IB-VIA_1-VIA_2 alloy and a group IIIA-VIA_1-VIA_2 alloy; and the at least one group IB-IIIA-VIA_1 ternary alloy of step (ii); and

   (iv) heat treating the second film of step ((iii)) to form a group IB-IIIA-VIA quaternary or higher alloy semiconductor film.

2. The method according to claim 1, wherein the mixture of the first film of step (ii) is a stable mixture such that the molar ratio of all the group IB-VIA_1 and/or group IIIA-VIA_1 alloys to all the at least one group IB-IIIA-VIA_1 ternary alloy remains substantially constant.

3. The method according to claim 1, wherein the metal film of step (i) is provided on a substrate optionally coated with a metal layer.

4. The method according to claim 3, wherein the metal layer is a Mo layer.

5. The method according to claim 1, wherein the metal film of step (i) comprises a mixture of metals selected from the group consisting of Cu, In and Ga.

6. The method according to claim 5, wherein the metal film of step (i) is a Cu-In-Ga alloy metal film.

7. The method according to claim 5, wherein the metal film is a Cu-In alloy metal film.

8. The method according to claim 1, wherein the group VIA_1 element is Se.

9. The method according to claim 1, wherein a source of the group VIA_1 element is a gaseous mixture of H_2Se and at least one inert gas.

10. The method according to claim 9, wherein the inert gas is Ar.

11. The method according to claim 9, wherein the molar concentration of Se relative to the at least one inert gas is from 0.01 to 15 molar percent.

12. The method according to claim 11, wherein the molar concentration of Se relative to the at least one inert gas is from 0.05 to 0.3 molar percent.

13. The method according to claim 1, wherein step (ii) is carried out at a reaction temperature from 300 to 500°C.

14. The method according to claim 13, wherein step (ii) is carried out at a reaction temperature from 350 to 450°C.

15. The method according to claim 13, wherein the metal film of step (i) is heated rapidly to a reaction temperature of between 300 to 500°C within 5 minutes.

16. The method according to claim 1, wherein during step (ii) the metal film of step (i) is exposed to the source of VIA_1 for a period from 10 to 120 minutes.

17. The method according to claim 16, wherein the metal film of step (i) is exposed to the source of VIA_1 for a period from 30 to 60 minutes.

18. The method according to claim 1, wherein the first film of step (ii) has below 50 atomic % of the $V1A_1$ element.

19. The method according to claim 8, wherein the first film of step (ii) has below 50 atomic % of Se.

20. The method according to claim 1, wherein the first film of step (ii) is treated under conditions to ensure that the mixture of the at least one binary alloy and the at least one group IB-IIIA-VIA_1 ternary alloy remains stable.

21. The method according to claim 20, wherein the source of the $V1A_1$ element is removed so as to maintain the stability of the mixture.

22. The method according to claim 20, wherein the first film of step (ii) is exposed to an inert atmosphere for 5 to 20 minutes.

23. The method according to claim 20, wherein the first film of step (ii) is cooled to temperatures below 200°C.

24. The method according to claim 5, wherein the first film of step (ii) comprises a mixture of at least one binary alloy selected from the

group consisting of InSe, CuSe and Ga_2Se_3 and at least one ternary alloy selected from the group consisting of $CuInSe_2$ and $CuGaSe_2$, where VIA_1 is Se.

25. The method according to claim 1 which is for producing a group IB-IIIA-VIA pentenary alloy semiconductor film, and wherein:

- step (i) comprises providing a metal film including a mixture of at least one group IB element, a first group IIIA element (the first group IIIA element hereinafter being referred to as $IIIA_1$) and a second group IIIA element (the second group IIIA element hereinafter being referred to as $IIIA_2$);

- step (ii) comprises heat treating the metal film of step (i) in the presence of a source of VIA_1 under conditions to form a first film comprising a mixture of binary alloys selected from the group consisting of a group IB-VIA_1 alloy, a group $IIIA_1$-VIA_1 alloy and a group $IIIA_2$-VIA_1 alloy and two ternary alloys, namely a group IB-$IIIA_1$-VIA_1 alloy and a group IB-$IIIA_2$-VIA_1 alloy;

- step (iii) comprises heat treating the first film of step (ii) in the presence of a source of VIA_2 under conditions to convert the first film of step (ii) into a second film comprising at least one alloy selected from the group consisting of a group IB-VIA_1-VIA_2 alloy, a group $IIIA_1$-VIA_1-VIA_2 and a group $IIIA_2$-VIA_1-VIA_2 alloy; and the ternary alloys of step (ii); and

- step (iv) comprises heat treating the second film of step (iii) to form a group IB-$IIIA_1$-$IIIA_2$-VIA_1-VIA_2 pentenary alloy semiconductor film.

26. The method of claim 25, wherein the first film of step (ii) includes a mixture of binary alloys in the form of a group IB-VIA_1 alloy, a group $IIIA_1$-VIA_1 alloy and a group $IIIA_2$-VIA_1 alloy and ternary alloys in the form of a group IB-$IIIA_1$-VIA_1 alloy and a group IB-$IIIA_2$-VIA_1 alloy and wherein the second film of step (iii) includes a

mixture of alloys in the form of a group IB-VIA_1-VIA_2 alloy, a group $IIIA_1$-VIA_1-VIA_2 and a group $IIIA_2$-VIA_1-VIA_2 alloy and the ternary alloys of step (ii).

27. The method according to claim 26, wherein step (iv) comprises a first heat treatment step wherein the second film of step (iii) is heated to form a third film comprising a mixture of quaternary alloys selected from the group consisting of a group IB-$IIIA_1$-VIA_1-VIA_2 alloy and a group IB-$IIIA_2$-VIA_1-VIA_2 alloy; and then subjecting the third film to a second heat treatment step wherein the third film is annealed so as to form a group IB-$IIIA_1$-$IIIA_2$-VIA_1-VIA_2 pentenary alloy semiconductor film.

28. The method according to claim 27, wherein the first heat treatment step of step (iv) comprises heating the second film of step (iii) in the presence of a source of VIA_2 so as to form the third film.

29. The method according to claim 28, wherein the second film of step (iii) is exposed to the source of VIA_2 for a period of from 5 to 10 minutes.

30. The method according to claim 29, wherein the first heat treatment step of step (iv) comprises heating the second film of step (iii) at a temperature from 450 to 600°C so as to form the third film.

31. The method according to claim 30, wherein the first heat treatment step of step (iv) comprises heating the second film of step (iii) at a temperature from 500 to 550°C.

32. The method according to claim 27, wherein the second heat treatment step of step (iv) comprises annealing the third film for 15 to 90 minutes.

33. The method according to claim 32, wherein the second heat treatment step of step (iv) comprises annealing the third film at a temperature from 500°C to 600°C.

34. The method according to claim 33, wherein the second heat treatment step of step (iv) comprises annealing the third film at a temperature from 520°C to 580°C.

35. The method according to either one of claims 26 and 27, wherein IB is Cu, $IIIA_1$ is In, $IIIA_2$ is Ga, VIA_1 is Se and VIA_2 is S.

36. The method according to claim 35, wherein the second heat treatment step of step (iv) comprises annealing the third film under conditions so as to form a pentenary alloy having the general formula II:

$$Cu(In_{1-x}Ga_x)(Se_{1-y}S_y)_2 \quad \ldots\ldots\ldots \quad (I)$$

37. The method according to claim 35, wherein a source of S is a gaseous mixture of H_2S and at least one inert gas.

38. The method according to claim 37, wherein the molar concentration of S relative to the at least one inert gas is from 0.1 to 10 molar percent.

39. The method according to claim 38, wherein the molar concentration of S relative to the at least one inert gas is from 0.3 to 0.5 molar percent.

40. The method according to claim 25, wherein, in step (iii), the first film of step (ii) is heat-treated at a temperature of from 100 to 500°C.

41. The method according to claim 40, wherein, in step (iii), the first film of step (ii) is heat-treated at a temperature of 450°C.

42. The method according to claim 40, wherein, in step (iii), the first film of step (ii) is heat-treated for a period of from 5 to 10 minutes.

43. The method according to claim 25 which is for producing a group IB-IIIA-VIA alloy semiconductor film, and wherein

- step (i) comprises providing a metal film comprising a mixture of Cu, In and Ga;

- step (ii) comprises heat treating the metal film in the presence of a gaseous mixture of H_2Se and at least one inert gas, wherein the molar concentration of Se relative to the at least one inert gas is from 0.05 to 0.3%, at a temperature of from 350°C to 450°C, for a period of between 30 to 60 minutes, so as to form a first film comprising a mixture of binary alloys in the form of CuSe, InSe, Ga_2Se_3 and the ternary alloys, namely $CuInSe_2$ and $CuGaSe_2$;

- step (iii) comprises heat treating the first film of step (ii) in the presence of a gaseous mixture of H_2S and at least one inert gas, at a temperature from 400°C to 500°C, for a period from 5 to 10 minutes, so as to form a second film comprising a mixture of sulfoselenides in the form of Cu(Se,S), In(Se,S) and Ga(Se,S) and the ternary alloys of step (ii); and

- step (iv) comprises heat treating the second film of step (ii) in the presence of H_2S in Ar, at a temperature of from 500°C to 550°C, for 5 to 10 minutes such that the sulfoselenides react with the ternary alloys of step (ii) to form a third film comprising a mixture of $CuIn(Se,S)_2$ and $CuGa(Se,S)_2$, and subsequently annealing the mixture of $CuIn(Se,S)_2$ and $CuGa(Se,S)_2$ at a temperature of from 520°C to 580°C so as to form a pentenary alloy having the general formula (I).

44. A method for producing a group IB-IIIA-VIA quaternary alloy semiconductor film, the method comprising the steps of:

(i) providing a metal film comprising a mixture of group IB and group IIIA metals;

(ii) heat treating the metal film in the presence of a source of a first group VIA element (said first group VIA element being hereinafter referred to as VIA_1) under conditions to form a first film comprising a mixture of at least one binary alloy selected from the group consisting of a group IB-VIA_1 alloy and a group IIIA-VIA_1 alloy; and at least one group IB-IIIA-VIA_1 ternary alloy, wherein the mixture is a stable mixture such that the molar ratio of all the group IB-VIA_1 and/or group IIIA-VIA_1 alloys to the at least one group IB-IIIA-VIA_1 ternary alloy remains substantially constant, and

(iv) heat treating the first film of step (ii) to form a group IB-IIIA-VIA quaternary alloy semiconductor film.

45. The method according to claim 44, wherein the first film of step (ii) is treated under conditions to ensure that the mixture of the at least one binary alloy and the at least one group IB-IIIA-VIA_1 ternary alloy remains stable.

46. The method according to claim 45, wherein the source of the VIA_1 element is removed so as to maintain the stability of the mixture.

47. The method according to claim 45, wherein the first film of step (ii) is exposed to an inert atmosphere for 5 to 20 minutes.

48. The method according to claim 45, wherein the first film of step (ii) is cooled to temperatures below 200°C.

49. The method according to claim 44, wherein the metal film of step (i) is provided on a substrate optionally coated with a metal layer.

50. The method according to claim 49, wherein the metal layer is a Mo layer.

51. The method according to claim 44, wherein the metal film of step (i) comprises a mixture of metals selected from the group consisting of Cu, In and Ga.

52. The method according to claim 51, wherein the metal film of step (i) is a Cu-In-Ga alloy metal film.

53. The method according to claim 51, wherein the metal film is a Cu-In alloy metal film.

54. The method according to claim 44, wherein the group VIA_1 element is Se.

55. The method according to claim 44, wherein a source of the group VIA_1 element is a gaseous mixture of H_2Se and at least one inert gas.

56. The method according to claim 55, wherein the inert gas is Ar.

57. The method according to claim 55, wherein the molar concentration of Se relative to the at least one inert gas is from 0.01 to 15 molar percent.

58. The method according to claim 57, wherein the molar concentration of Se relative to the at least one inert gas is from 0.05 to 0.3 molar percent.

59. The method according to claim 44, wherein step (ii) is carried out at a reaction temperature from 300 to 500°C.

60. The method according to claim 59, wherein step (ii) is carried out at a reaction temperature from 350 to 450°C.

61. The method according to claim 59, wherein the metal film of step (i) is heated rapidly to a reaction temperature of between 300 to 500°C within 5 minutes.

62. The method according to claim 44, wherein during step (ii) the metal film of step (i) is exposed to the source of VIA_1 for a period from 10 to 120 minutes.

63. The method according to claim 62, wherein the metal film of step (i) is exposed to the source of VIA_1 for a period from 30 to 60 minutes.

64. The method according to claim 44, wherein the first film of step (ii) has below 50 atomic % of the $V1A_1$ element.

65. The method according to claim 54, wherein the first film of step (ii) has below 50 atomic % of Se.

66. The method according to claim 44, wherein the first film of step (ii) comprises a mixture of at least one binary alloy selected from the group consisting of InSe, CuSe and Ga_2Se_3 and at least one ternary alloy selected from the group consisting of $CuInSe_2$ and $CuGaSe_2$, where VIA_1 is Se.

67. The method according to claim 44 which is for producing a group IB-IIIA-VIA quaternary alloy semiconductor film, and wherein:

- step (i) comprises providing a metal film including a mixture of at least one group IB element, a first group IIIA element (the first group IIIA element hereinafter being referred to as $IIIA_1$) and a second group IIIA element (the second group IIIA element hereinafter being referred to as $IIIA_2$);

- step (ii) comprises heat treating the metal film of step (i) in the presence of a source of VIA_1 under conditions to form a first film comprising a mixture of binary alloys selected from the group consisting of a group $IB\text{-}VIA_1$ alloy, a group $IIIA_1\text{-}VIA_1$ alloy and a group $IIIA_2\text{-}VIA_1$ alloy and a ternary alloy being a group $IB\text{-}IIIA_1\text{-}VIA_1$ alloy;

- step (iv) comprises heat treating the first film of step (ii) to form a group $IB\text{-}IIIA_1\text{-}IIIA_2\text{-}VIA_1$ quaternary alloy semiconductor film.

68. The method according to claim 67, wherein the heat treatment of step (ii) is carried out at a reaction temperature of 400°C.

69. The method according to claim 67, wherein step (iv) comprises a first heat treatment step wherein the first film of step (ii) is heated and then subsequently a second heat treatment step wherein the first film is annealed so as to form a group $IB\text{-}IIIA_1\text{-}IIIA_2\text{-}VIA_1$ quaternary alloy semiconductor film.

70. The method according to claim 69, wherein the first heat treatment step of step (iv) comprises heating the first film of step (ii) to a reaction temperature of from 100 to 600°C.

71. The method according to claim 69, wherein the second heat treatment step of step (iv) comprises first annealing the first film of step (ii) in the presence of an inert gas and then subsequently annealing the first film in the presence of a source of VIA_1.

72. The method according to claim 71, wherein the first film of step (ii) is first annealed in the presence of the inert gas at a temperature of from 100 to 600°C.

73. The method according to claim 72, wherein the first film of step (ii) is first annealed in the presence of the inert gas at a temperature of from 500 to 550°C.

74. The method according to claim 72, wherein the first film is fist annealed in the presence of the inert gas for a period of from 10 to 60 minutes.

75. The method according to claim 71, wherein the first film of step (ii) is subsequently annealed in the presence of a source of VIA_1 for at least 30 minutes.

76. The method according to claim 75, wherein the first film of step (ii) is annealed in the presence of a source of VIA_1 at a temperature of 500°C.

77. The method according to either one of claims 67 and 69, wherein IB is Cu, $IIIA_1$ is In, $IIIA_2$ is Ga, VIA_1 is Se.

78. The method according to claim 77, wherein the quaternary alloy has a formula (II)

$$Cu(InGa)Se_2 \ldots\ldots \quad (II)$$

79. The method according to claim 77, wherein a source of Se is a gaseous mixture of H_2Se and at least one inert gas.

80. The method according to claim 79, wherein the molar concentration of Se relative to the at least one inert gas is 0.12%.

81. The method according to claim 67 which is for producing a group IB-IIIA-VIA quaternary alloy semiconductor film, and wherein:

- step (i) comprises providing a metal film comprising a mixture of Cu, In and Ga in elemental or alloy form;

- step (ii) comprises heat treating the metal film in the presence of a gaseous mixture of H_2Se and at least one inert gas, wherein the molar concentration of Se relative to the at

least one inert gas is from 0.05 to 0.3%, at a temperature of 400°C, for a period of between 30 to 60 minutes, so as to form a mixture of binary alloys in the form of CuSe, InSe, Ga_2Se_3 and a ternary alloy in the form of a $CuInSe_2$ alloy.

- step (iv) comprises subjecting the first film of step (ii) to the following consecutive steps:

    - a first heat treatment step comprising heat treating the first film of step (ii) to a reaction temperature from 500°C to 550°C in 15 to 30 minutes;

    - a second heat treatment step comprising first annealing the first film of step (ii) in Ar(g) at a reaction temperature from 500°C to 550°C for at least 15 minutes; and then secondly annealing the first film of step (ii) in the presence of a gaseous mixture of H_2Se and Ar(g), wherein the molar concentration of Se relative to Ar is 0.12% so as to form a quaternary alloy having the general formula (II).

82 The method according to claim 44, which is for producing a group IB-IIIA-VIA quaternary alloy semiconductor film, and wherein:

- step (i) comprises providing a metal film including a mixture of at least one group IB element and a group IIIA element;

- step (ii) comprises heat treating the metal film of step (i) in the presence of a source of VIA_1 under conditions to form a first film comprising a mixture of binary alloys selected from the group consisting of a group IB-VIA_1 alloy, a group IIIA-VIA_1, and a ternary alloy being a group IB-IIIA-VIA_1 alloy; and

- step (iv) comprises heat treating the first film of step (ii) in the presence of a source of VIA_2 so as to form a group IB-IIIA-VIA_1-VIA_2 quaternary alloy semiconductor film.

83 The method according to claim 82, wherein step (iv) comprises a first heat treatment step wherein the first film of step (ii) is heated and then subsequently a second heat treatment step wherein the first film of step (ii) is annealed so as to form a group IB-IIIA-VIA_1-VIA_2 quaternary alloy.

84. The method according to claim 83, wherein the first heat treatment step of step (iv) comprises heating the first film of step (ii) to a reaction temperature from 100 to 600°C.

85. The method according to claim 83, wherein the second heat treatment step of step (iv) comprises annealing the first film of step (ii) in the presence of a source of VIA_2.

86. The method according to claim 85, wherein the first film of step (ii) is annealed in the presence of the source of VIA_2 at a temperature from 100 to 600°C.

87. The method according to claim 86, wherein the first film of step (ii) is annealed in the presence of the source of VIA_2 at a temperature from 500 to 550°C.

88. The method according to claim 87, wherein the first film of step (ii) is annealed in the presence of a source of VIA_2, at a temperature of 500°C.

89. The method according to claim 85, wherein the first film of step (ii) is annealed in the presence of a source of VIA_2 for at least 30 minutes.

90. The method according to either one of claims 82 and 83, wherein IB is Cu, the group IIIA element is In, VIA_1 is Se, VIA_2 is S.

91. The method according to claim 90, wherein the quaternary alloy has a formula (III);

$CuIn(Se_{1-y}S_y)_2$.....(III)

92. The method according to claim 90, wherein a source of S is a gaseous mixture of H_2S and at least one inert gas.

93. The method according to claim 92, wherein the molar concentration of S relative to the at least one inert gas is 0.35 molar percent.

94. The method according to claim 82, which is for producing a group IB-IIIA-VIA quaternary alloy semiconductor film, and wherein:

- step (i) comprises providing a metal film comprising a mixture of Cu and In in elemental or alloy form;

- step (ii) comprises heat treating the metal film in the presence of a gaseous mixture of H_2Se and at least one inert gas, wherein the molar concentration of Se relative to the at least one inert gas is from 0.05 to 0.3% for a period of between 30 to 60 minutes, so as to form a mixture of binary alloys in the form of CuSe and InSe and a ternary alloy, namely $CuInSe_2$; and

- step (iv) comprises subjecting the first film of step (ii) to the following consecutive steps:

    - a first heat treatment step comprising heat treating the first film of step (ii) to a reaction temperature from 500°C to 550°C in 15 to 30 minutes;

        - a second heat treatment step comprising annealing the first film of step (ii) in the presence of a gaseous mixture of H2S and Ar(g), at a temperature of from 500oC to 550oC, wherein the molar concentration of S relative to Ar is 0.35%

so as to form a quaternary alloy having the general formula (III).